[Contribution from the Chemical Laboratory, University of Wisconsin.]

A STUDY OF THE PREPARATION OF CERTAIN ORGANIC SALTS OF TELLURIUM.[1]

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In an investigation described elsewhere[2] it was necessary to secure solutions of tellurium in a number of non-aqueous solvents. This led to an investigation of certain organic salts of tellurium since, in many cases, combinations of a metal with an organic acid radical are more likely to be dissolved by organic liquids than are inorganic salts. Although tellurium dioxide is chiefly acid in character, there are numerous cases where it shows specific basic tendencies. This suggested a general method for the preparation of organic salts of tellurium, namely, the treatment of tellurium dioxide with the free organic acid. In some cases this proved to be a satisfactory method of preparation, while in numerous other cases, a chemical union could not be brought about by this means. This was especially true where the acid character of the organic acid was unusually weak.

Experimental.

Tellurium Acid Tartrate.—It was known to Berzelius[3] that tellurium dioxide could be dissolved in tartaric acid and a salt separated out in which tellurium acted as a base. Becker further studied this reaction and reported[4] that if a solution of tellurium dioxide in tartaric acid was allowed to evaporate spontaneously in the air, long, radiating, colorless crystals separated out which his analysis showed to be tellurium acid tartrate, $Te(HC_4H_4O_6)_4$. Becker[5] states it is very difficult to separate these crystals from the tartaric acid itself.

In the present work, the preparation of the salt consisted in treating a solution of tartaric acid, saturated at 20° C., with an excess of purified tellurium dioxide which had been ground to pass a 200-mesh sieve. The mixture was contained in an Erlenmeyer flask fitted with a one-holed rubber stopper in order to minimize evaporation and was heated in a sand bath at a temperature of 70° C. At the end of three days, reaction had taken place as evidenced by a decrease in the quantity of the dioxide, while a small amount of elementary tellurium had separated out.

After prolonged heating at this temperature, a portion of the liquid was filtered and the materials in solution allowed to crystallize. After

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[1] Abstract of a part of a thesis submitted to the graduate school of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This Journal, 41, 300 (1919).

[3] Berzelius, *Pogg. Ann.*, 8, 411 (1826).

[4] Becker, *Ann.*, 180, 257 (1876).

[5] Becker, *Loc. cit.*

being freed from the mother liquor as completely as possible by pressing between filter paper, an analysis of the colorless crystals showed them to contain 5.60% tellurium. The formula $Te(HC_4H_4O_6)_4$ requires 17.62% tellurium. The flask containing the dioxide and tartaric acid was heated again for two months longer at 70° C. and crystallization allowed to take place at room temperature, since if the solution is boiled the tellurium will slowly but completely precipitate as the element. The crystals separating out proved to contain 16.38% tellurium, which is approximately the theoretical percentage required.

The reaction taking place between tellurium dioxide and tartartic acid may be summarized as follows: A strong solution of tartaric acid slowly dissolves tellurium dioxide with the formation of tellurium acid tartrate. Inasmuch as the solubility of the free acid and newly formed salt are very nearly the same, it is impossible to separate them by this means. It consequently becomes necessary to continue the reaction to completion. Heating accelerates the reaction, but a boiling temperature must be avoided as it will cause the separation of tellurium in the elementary form.

Tellurium Acid Citrate.—Since tellurium was able to replace one of the two hydrogen atoms of the dibasic tartaric acid, it was interesting to determine the number of hydrogen atoms this element was able to replace in a tribasic organic acid. Preliminary experiments showed tellurium dioxide to be slowly dissolved by citric acid. Tellurium dioxide and a solution of citric acid were heated together for one month in a manner similar to the procedure just described. During this time no elementary tellurium was set free as in the case with tartaric acid. Crystals separating out from the supernatant liquid after concentration on a hot plate were of two different types. They consisted of large, colorless crystals which were recognized as crystals of citric acid, and some small, white, opaque crystals. An analysis of the latter showed a content of 9.73% tellurium. By dissolving the small, white, opaque crystals in distilled water and recrystallizing, it was found that similar crystals separated first and others of citric acid later. An analysis of the former showed them to contain 21.25% tellurium. Fractional crystallization was therefore continued. The results of the analyses carried out with each fraction of crystals are arranged in the accompanying table:

Fraction.	Wt. sample. G.	Wt. Te found. G.	Te. %.
1	0.6133	0.0509	9.73
2	0.5270	0.1120	21.25
3	0.5793	0.1394	24.07
4	0.5439	0.1333	24.50
5	0.3264	0.0819	25.09

Since the percentage of tellurium required for the formula $Te(HC_6H_5O_7)_2$

is 25.10%, it appears that this compound is produced by the action of citric acid on tellurium dioxide. Tellurium acid citrate may be described as a white, opaque, finely crystalline compound which tends to separate in small, radiating clusters. In comparing its preparation with that of the acid tartrate, it is of interest to note that its solution in water will withstand boiling temperatures without reduction to the element. Its solubility is sufficiently less than that of citric acid to permit its complete separation from the free acid.

Tellurium Oxalate.—If tellurium dioxide is heated with a saturated solution of oxalic acid, a certain amount of tellurium is held in solution as shown by tests for the element. If such a solution is allowed to crystallize spontaneously in the air, a mixture of crystals of the dioxide and acid separate. There seems, therefore, to be no compound existing between tellurium and the oxalic acid radical. Klein[1] obtained similar results when he attempted to prepare a double oxalate of potassium and tellurium.

Tellurium Succinate.—A solution of succinic acid was heated with finely divided tellurium dioxide for three months. At no time did a portion of the filtered solution respond to a test for tellurium. There is apparently no action between tellurium dioxide and succinic acid.

Tellurium Dioxide and Certain Other Organic Acids.—An excess of tellurium dioxide was also heated with concentrated solutions of malic, gallic and lactic acids for long periods of time. All of these acids slowly dissolved small amounts of tellurium dioxide. In the case of malic and gallic acids, crystals could be obtained which contained small amounts of tellurium, but it was impossible to separate the tellurium containing substances from the free acid. The solution obtained in lactic acid failed to yield any crystals after concentration by various methods. It was evident that if a definite compound was formed, it was soluble in the liquid lactic acid. In none of these cases was there a separation of elementary tellurium during the long periods of heating, as was the case with tartaric acid.

Klein[2] had similar experience with tellurium dioxide and phosphoric acid. A reaction between these two compounds could be recognized. He states, however, he was entirely unable to separate out a definite compound containing tellurium and phosphoric acid.

Tellurium Oleate.—Tellurium tetrachloride proved to be easily soluble in anhydrous benzene. Kahlenberg[3] has shown that if a solution of copper oleate in benzene is treated with a metallic chloride dissolved in benzene, a brown precipitate of anhydrous copper chloride is produced with the metallic oleate. This suggested a means of preparation of tel-

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[1] *Ann. chim. phys.*, [6] **10**, 108 (1887); *Bull. soc. chim.*, **45**, 714.

[2] Klein, *Loc. cit.*

[3] Kahlenberg, *Jour. Phys. Chem.*, **6**, 1 (1902).

lurium oleate and certain other compounds of tellurium with the higher fatty acids.

A solution of purified copper oleate in anhydrous benzene was treated with an excess of a solution of tellurium tetrachloride in benzene. A precipitate of brown anhydrous copper chloride immediately formed. The precipitate was gelatinous and extremely difficult to filter. Before filtration could be effected, a purple color developed in the solution and in the precipitate. This indicated that if tellurium oleate had originally been formed, it rapidly dissociated into colloidal tellurium and free oleic acid.

Various attempts were made to salt out an oleate of tellurium from the solution immediately after precipitation. As "salting out" agents, water, as well as organic liquids in which the metallic oleates are usually insoluble, were used, but the tellurium always separated in the elementary form before a definite compound could be obtained.

Final attempts were made by using molecular proportions of the two reagents dissolved in benzene. The benzene was carefully removed at a temperature not exceeding 65° C. The remaining black residue consisted of a mixture of free oleic acid, copper chloride, and elementary tellurium.

It is therefore evident that these methods do not offer a means of preparation of this compound. Results show that tellurium oleate is probably produced but tellurium and oleic acid are so weakly basic and acid, respectively, that the compound immediately dissociates into elementary tellurium and free oleic acid.

A number of similar experiments were carried out with copper stearate solutions but with identical results.

Summary.

1. A detailed method for the preparation of tellurium acid tartrate has been given. It was found that this salt cannot be separated from tartaric acid by crystallization. This is contrary to the findings of Becker.

2. Tellurium acid citrate—$Te(HC_6H_5O_7)_2$, is produced by the action of a concentrated solution of citric acid on tellurium dioxide. This salt crystalllzes in white, opaque, radiating crystals. It differs from the acid tartrate in that its solutions will withstand boiling temperatures without reduction and its solubility is sufficiently less than that of the free acid to permit purification by fractional crystallization.

3. Succinic acid does not attack tellurium dioxide.

4. Oxalic, lactic, malic and gallic acids hold appreciable amounts of tellurium dioxide in solution. It was impossible to separate a crystalline compound of tellurium with any of these acids.

5. The existence of an oleate or stearate of tellurium has been shown to be doubtful.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF CASEIN AND PEPTONE.

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To understand many of the problems of physiological chemistry, a knowledge of molecular forces in solutions has become of greater and greater importance. Surface tension has, especially in the recent times, been considered as one of the forms of expression of these forces. However, in the case of the more or less colloidal solutions in question, this property is frequently very difficult to measure; in most solutions of proteins, split proteins, and similar substances, the surface tension is lowered with rising concentration, and the substance will therefore, according to Gibbs' rule, accumulate, sometimes to a very high degree, in the surface, where it furthermore often coagulates, forms films, etc.

For that reason it would be advantageous to investigate a property, which, like the surface tension, might be expected to give information as to the molecular conditions, and which could be measured without the difficulties arising from the peculiar state of the surface. Such a property is compressibility, which gives an expression of the state of all the molecules in the solution, not only those in the surface. As mentioned in a foregoing paper,[1] in such solutions the relation between the surface tension and the compressibility does not seem at first to be very plain, because of the changing nature of the solvent; but whether or not the relation between the two properties is clear and simple the compressibility is nevertheless such an important property that it may be able to furnish valuable information as to the internal structure and behavior of physiologically interesting solutions.

As regards the compressibility of colloidal solutions, very few measurements have been published; and nobody has, so far as I know, measured both the surface tension and the compressibility of identical solutions. Comparison of data from different sources, on account of the very uncertainly defined composition of the colloids employed. could hardly be of great value.

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[1] Richards and Palitzsch, "Compressibility of Urethane Solutions, Etc.," THIS JOURNAL, 41, 59 (1919).